DIRECT COAL LIQUEFACTION:
A POTENTIAL ROUTE TO THERMALLY STABLE JET FUEL

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INTRODUCTION

The principal mechanism of fuel degradation at temperatures above 300°C is pyrolytic decomposition. Cycloalkanes are much more resistant to thermal degradation than are n-alkanes or alkylaromatics [1]. Indeed, decalin shows remarkable thermal stability even at 450° [1, 2]. Hydroaromatics, such as tetralin, are also quite stable at these temperatures when reacted neat [1, 2] and can suppress the thermal degradation of other compound classes, such as n-alkanes, in a process termed hydrogen-transferring pyrolysis [3, 4]. Thus high concentrations of cycloalkanes and hydroaromatics in a real fuel (which of course may contain dozens of components) could provide significant thermal stability.

Direct liquefaction of coal could potentially provide a facile route to liquids boiling in the jet range and containing the desired cycloalkanes and hydroaromatics. The key chemical steps in this process would be the liberation of the aromatic units by cleavage of whatever crosslinks or other interactions hold them in the coal structure, and the hydrogenation of the aromatics to cycloalkanes or hydroaromatics. Clearly, coals showing good reactivity during liquefaction are desirable. To facilitate liberation of the aromatic ring systems, it would be helpful to select coals containing a relatively low population of crosslinks. To minimize downstream processing, it would also be useful to select coals in which a preponderance of the aromatic structures are naphthalene derivatives, to allow direct hydrogenation to decalins and tetralins. Similarly, it would be desirable to have a low content of heteroatoms, also to minimize downstream treatment of the liquids. Not all of these features are available in coals of a given rank. High reactivity and small aromatic units are characteristics of coals at the low end of the rank range. Low crosslink density and relatively low heteroatom content are more likely to be found in the bituminous rank range. Thus the selection of potential feedstocks may involve a compromise to achieve a reasonable balance among these desired characteristics.

We are conducting an exploratory study to test the hypothesis that it is possible to form high yields of cycloalkanes and hydroaromatics boiling in the jet range by selection of feedstocks to contain a high proportion of small aromatic units and relatively few crosslinks; and by choosing catalyst and reaction conditions to liberate the desirable structural features of the coal. In the present paper we report results of reactions of two bituminous coals subjected to temperature-programmed liquefaction, particularly, the effects of coal, solvent, and catalyst on conversion, product slate, and product quality.

EXPERIMENTAL

The coals were obtained from the Penn State Coal Sample Bank and Data Base. The provenance and characteristics of the coals are shown in Table 1. The solvents, catalysts, and reagents used in this work were purchased from commercial vendors and used without further purification.

Liquefaction reactions were conducted in stainless steel microautoclave reactors of nominal 30 mL capacity. Pyrene and 9,10-dihydrophenanthrene (DHP) were used as liquefaction solvents. The reactors were charged with 4 g coal and 4g of the desired solvent. For those reactions in which a catalyst was used, coal was dried and impregnated with ammonium tetrathiomoybdate (ATTM) or $NiCl_2$ as described in previous work [5]. The

reactors were pressurized to 7 MPa with H_2 at ambient temperature. The concept of temperature-programmed liquefaction has been discussed elsewhere [5, 6]. Briefly, the reactor is immersed in a sandbath preheated to 200°C and held for 15 min. The temperature is then ramped to 425° at 7°/min, and is held at 425° for 30 or 60 min. At the end of a reaction, the reactor is quenched by immersion in cold water.

Products were emptied from the tubing bomb into a dry tared thimble using dichloromethane (DCM) and extracted with DCM for about 36-48 h until the extracted solvent appeared clear. The products were then extracted with tetrahydrofuran (THF) for about 24–36 h until the extracted solvent appeared clear. The DCM was rotoevaporated from the DCM-solubles, and then the sample was extracted with hexane. The THF-insoluble portion was rinsed with acetone and pentane and dried at 100°C for 12 h. The THF-soluble fractions were dried for 1 h at 60°C. The hexane-soluble fractions were analyzed by GC/FID and GC/MS. The conditions of the GC used were a rate of 4 °C/min from 40 to 280 °C.

RESULTS AND DISCUSSION

The principal experimental results are summarized in Table 2. The DCM-solubles include gas yields, and gas yields were ≤5% for all reactions. The principal compound classes identified in the hexane-soluble portions of the DCM-soluble products are summarized in Table 3. For convenience, we will occasionally refer to three ratios: a) THF-solubles to the sum of the DCM-solubles expressed as THF/DCM; b) aromatic compounds of one ring to those with two rings or more, (i.e., benzenes + phenols to naphthalenes + phenanthrenes + polynuclear aromatics) expressed as B+P/≥2-ring; and c) the total aromatic compounds to alkanes, expressed as ΣAro/ΣAli.

For reactions without catalyst, conversions to DCM-solubles depend mainly on solvent. For a given solvent, conversions of the two coals are similar. However, DHP is clearly superior to pyrene for increasing conversions. Even though pyrene is well known as a hydrogen shuttler [7], DHP is a potent hydrogen donor [8]. Furthermore, in non-catalytic reactions, most of the hydrogen consumption comes from the solvent rather than gas-phase H_2 [8], so it is not surprising that substantially higher conversions are achieved in DHP. Although the conversions of the two coals in a given solvent are comparable, and the comparative effects of pyrene versus DHP are comparable, the change in product slates with increased conversion is quite different between the two coals. With DECS-6, the increased conversion effected by DHP comes largely via formation of THF-solubles. THF/DCM increases from 0.23 for reaction in pyrene to 0.64 for reaction in DHP. In contrast, THF/DCM is essentially unchanged (and in fact slightly decreases from 0.37 to 0.33) for reactions of DECS-12 in these solvents. DHP reduces the proportion of aromatics with ≥2 rings in the DCP-solubles, and increases the proportion of total aromatics relative to alkanes, relative to results obtained using pyrene. For DECS-6, the B+P/≥2-ring ratio is 0.98 for reaction in pyrene, and 0.73 for reaction in DHP. ΣAro/ΣAli increases from 1.46 to 1.80 for reaction in pyrene and DHP, respectively. The effect of solvent on the B+P/≥2-ring ratio for DECS-12 is quite similar, 1.19 for reaction in pyrene decreasing to 0.83 when DHP is used. A remarkable difference is seen in the ΣAro/ΣAli ratio for DECS-12 relative to DECS-6. For both coals, reaction in DHP increases this ratio relative to reaction in pyrene, but the products from reaction of DECS-12 have so few n-alkanes that there is an order-of-magnitude difference in the ΣAro/ΣAli ratios. Characterization of these two coals by flash pyrolysis GC/MS has shown the preponderence of n-alkanes in DECS-6 relative to DECS-12 [9].

For reactions in pyrene, the addition of catalyst not unexpectedly enhances conversion of both coals. Using either MoS_2 or $NiCl_2$, the conversion of DECS-6 increases by about 30 percentage points (Table 2). Both catalysts increase the conversion in the hydrogen-shuttling solvent pyrene to the same level as obtained by using the strong hydrogen donor solvent DHP without catalyst. However, the two catalysts have quite different effects on the product slate. MoS_2, which could be considered to be a hydrogenation catalyst [10-12], provides a very high yield of light products, THF/DCM being only 0.06. In comparison, $NiCl_2$, a cracking

catalyst [12-13] provides almost the same conversion, but a higher yield of preasphaltenes than attained with MoS_2. Using $NiCl_2$ catalyst, the THF/DCM ratio is about the same as obtained in pyrene but without catalyst, i.e., 0.19 vs. 0.23, respectively. Thus $NiCl_2$ appears to increase the depolymerization of DECS-6, but not to alter the relative proportion of products; in comparison, MoS_2 seems both to increase the depolymerization and shift the product slate toward lighter products.

However, when deductions are drawn based on conversion data, it is important not to lose sight of the fact that these product classifications are based on solubility behavior, which potentially could mask differences in molecular composition. For $NiCl_2$/pyrene reaction of DECS-6, there is a substantial increase in the amount of naphthalenes in the DCM-solubles relative to the MoS_2-catalyzed reaction, which actually decreases the B+P/≥2-ring ratio, from 1.87 for MoS_2 catalysis to 1.32 with $NiCl_2$. With DECS-12, catalytic reaction in pyrene also increases conversion to about the same value as obtained in non-catalytic reaction in DHP. Use of MoS_2 shifts the product slate to lighter products, as occurred with DECS-6, although the effect is not quite so pronounced for DECS-12, THF/DCM decreasing from 0.37 to 0.23. With $NiCl_2$, however, the proportion of preasphaltenes in the product is actually enhanced relative to reaction without catalyst. In this case the effect of $NiCl_2$ catalysis is quite different for the two coals. However, when product composition is examined, a reduction of the B+P/≥2-ring ratio is observed for $NiCl_2$-catalyzed reaction of DECS-12 in pyrene relative to MoS_2, which can, as in the similar case of DECS-6, be attributed to a large increase in naphthalenes and a loss of phenols in the DCM-solubles. It is possible that the reduction of phenols and the concurrent increase in THF/DCM ratio could mean that retrogressive reactions are promoted by the $NiCl_2$ cracking without the stabilization of hydrogen from an H-donor or hydrogenation catalyst.

The effect of reaction time was evaluated only for DECS-6, by comparing reactions with high-temperature holding times of 30 and 60 min for both MoS_2 and $NiCl_2$ in pyrene. Little change was observed in either conversion or product slate. It is unlikely that the slight changes in conversion or product slate observed after 60 min would repay the additional processing costs associated with a doubling of the residence time at 425°.

The combination of the MoS_2 hydrogenation catalyst and DHP donor solvent in reaction of DECS-6 provided the highest conversion observed in the present work, 95%. The product slate was about the same as that obtained for MoS_2 and pyrene, with THF/DCM of 0.06. Liquefaction of DECS-6 in DHP without catalyst actually increased the THF/DCM ratio relative to non-catalytic reaction in pyrene. The catalytic effect of the added MoS_2 thus seems important for shifting the product slate to lighter—on the basis of solubility classifications—products, regardless of whether a hydrogen donor or hydrogen shuttler is used as solvent. Using DHP with $NiCl_2$ produced no increase in conversion relative to that of $NiCl_2$ and pyrene. There is, though, a shifting of the THF/DCM ratio to 0.15, compared with 0.19 for $NiCl_2$/pyrene, and 0.23 for non-catalytic reaction in pyrene. It is noteworthy that the combination of catalyst and donor solvent produces the lowest values of the B+P/≥2-ring ratio observed for this coal, 0.46 for MoS_2-catalysis and 0.53 for $NiCl_2$. Thus 40–43% of the DCM-solubles from DECS-6 for catalytic reaction in DHP are naphthalene derivatives.

For liquefaction of DECS-12 in pyrene, $NiCl_2$ provided higher conversions than MoS_2, 84 vs 77%, respectively. The same superiority of $NiCl_2$ is observed when DHP is used as the solvent, the conversions being 89 and 85%, respectively. For both coals, a change of solvent from pyrene to DHP when MoS_2 is used as the catalyst produces essentially the same effect: an additional 6-8 percentage points of conversion, and a reduction of THF/DCM to 0.06. On the other hand, the change of solvent has different effects for the coals when $NiCl_2$ is used as the catalyst. We discussed the DECS-6 case above; for DECS-12, an increase in conversion and significant shift of THF/DCM is observed when DHP is used instead of pyrene. The combination of a catalyst and donor solvent causes significant reductions in the B+P/≥2-ring ratio, as was seen for DECS-6. Indeed, nearly 50% of the DCM-solubles from MoS_2/DHP reaction of DECS-12 are naphthalene derivatives.

An additional aspect of $NiCl_2$ catalysis is its ability to reduce yields of phenols relative to similar reactions in the presence of MoS_2. For all but one coal/solvent combination, the concentration of phenols in the DCM-solubles is lower for the $NiCl_2$-catalyzed reaction relative to MoS_2, the single exception being DECS-6/DHP. But if there is a reduction in phenols when using $NiCl_2$, and a concurrent increase in THF/DCM, it could be the lost phenols are participating in retrogressive reactions by crosslinking to THF-solubles. Soloman et al. [14] have suggested that functional groups containing oxygen participate in retrogressive reactions. It is also apparent these crosslinking reactions are repressed when a donor solvent or a good hydrogenation catalyst is used.

Attaining the highest conversion with either coal under these reaction conditions clearly requires the presence of the donor solvent in addition to a catalyst. For DECS-6, 95% conversion is achieved for MoS_2/DHP reaction. Any other combination of solvent, catalyst, or both provides conversions in the range 83–89%. For DECS-12, the highest conversion, 89%, was obtained in $NiCl_2$/DHP reaction; the other combinations of solvent and catalyst gave conversions of 77–85%. For either coal and either solvent, the lowest values of THF/DCM are invariably obtained with MoS_2 catalysis. THF/DCM ratios of 0.06 can be achieved for either coal with this catalyst, along with conversions in the 85–95% range. Furthermore, MoS_2/DHP liquefaction produces DCM-solubles that are 40–50% naphthalene derivatives. The subsequent hydrogenation of this product could, in principle, provide a liquid that contains ~50% of the desirable, high-thermal-stability decalins and tetralins.

SUMMARY AND CONCLUSIONS

This paper reports preliminary results of work still in progress. We have so far shown that, with careful selection of the feedstock, it is possible to achieve 85–95% conversions, with THF/DCM ratios <0.1 and 40-50% of the DCM-solubles being naphthalenes. We have not yet attempted to improve these results by optimizing reaction conditions. The DCM-solubles are highly aromatic, with $\Sigma Aro/\Sigma Ali$ approaching 30 for some reactions of DECS-12. It is clear that both a hydrogenation of the product and a hydrodeoxygenation to remove phenols, neither of which is an insignificant operation, still must be investigated. Nevertheless, if these two further transformations can be effected, either by some alteration of reaction strategy such as "reverse temperature staging" [15] or by separate subsequent reactions, the prospect exists for direct conversion of bituminous coals to high yields of liquids containing high concentrations of desirable decalins and tetralins. Such a product could be the foundation of a jet fuel with excellent high-temperature stability characteristics.

ACKNOWLEDGEMENT

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Table 1: Properties of coals.

Coal Number	DECS-6	DECS-12
Seam, State	Blind Canyon	Pittsburgh #8, PA
Rank	hvA b	hvA b
%C	81.72	84.75
%O	10.10	7.37
%H	6.22	5.66
%S	0.40	0.83
%N	1.56	1.40
%Mineral Matter	6.67	11.88
H/C	0.905	0.794

Table 2: Liquefaction conversion data for DECS-6 and DECS-12.

Expt #	Temp	Catalyst	Solvent	TC	THF-Sol	DCM-Sol	THF/DCM
tb 6-8	TPL, 425-30	none	pyrene	55.2	10.5	44.7	0.235
tb 6-9	TPL, 425-30	none	DHP	83.0	32.5	50.5	0.644
tb 6-3	TPL, 425-30	MoS_2	pyrene	89.3	5.1	84.2	0.061
tb 6-4a	TPL, 425-30	$NiCl_2$	pyrene	83.0	13.1	69.9	0.187
tb 6-10	TPL, 425-30	MoS_2	DHP	95.0	5.7	89.3	0.064
tb 6-11	TPL, 425-30	$NiCl_2$	DHP	83.2	11.0	72.2	0.152
tb 6-6	TPL, 425-60	MoS_2	pyrene	88.2	3.6	84.6	0.043
tb 6-7	TPL, 425-60	$NiCl_2$	pyrene	87.3	12.7	74.6	0.170
tb 12-5	TPL, 425-30	none	pyrene	51.9	14.0	37.9	0.369
tb 12-6	TPL, 425-30	none	DHP	81.7	20.1	61.6	0.326
tb 12-3	TPL, 425-30	MoS_2	pyrene	76.8	14.5	62.3	0.233
tb 12-4	TPL, 425-30	$NiCl_2$	pyrene	84.2	28.3	55.9	0.506
tb 12-7	TPL, 425-30	MoS_2	DHP	85.4	5.1	80.3	0.064
tb 12-8	TPL, 425-30	$NiCl_2$	DHP	88.7	13.1	75.6	0.173

TC = total conversion
DCM-Sol = DCM-Solubles + Gas Yield
THF/DCM = ratio of THF-Solubles to DCM-Solubles

Table 3: Percent area of major compounds in GC of hexane-solubles.

Expts	Benzenes	Phenols	2-Ring	3-Ring	4-Ring +	Alkanes	B+P/2-Ring	ΣAro/ΣAli
tb 6-8	3.7	25.6	27.7	2.3	0.0	40.6	0.98	1.46
tb 6-9	8.9	18.2	35.4	n.d.	1.8	35.8	0.73	1.80
tb 6-3	14.6	30.6	21.0	3.2	0.0	30.5	1.87	2.28
tb 6-4	19.2	25.8	29.4	3.8	0.9	21.0	1.32	3.77
tb 6-10	0.5	19.4	40.5	n.d.	3.1	36.6	0.46	1.73
tb 6-11	2.6	20.5	43.4	n.d.	0.0	33.4	0.53	1.99
tb 6-6	2.7	44.7	22.8	3.9	2.9	23.0	1.60	3.35
tb 6-7	8.6	29.5	34.5	3.9	0.0	23.5	0.99	3.26
tb 12-5	8.3	41.8	20.7	20.8	0.6	7.8	1.19	11.8
tb 12-6	15.4	28.3	46.7	n.d.	6.2	3.3	0.83	29.3
tb 12-3	5.0	46.4	29.2	2.2	4.5	12.8	1.43	6.82
tb 12-4	6.3	32.2	38.6	6.6	4.4	11.9	0.78	7.40
tb 12-7	2.4	30.1	48.1	n.d.	10.4	9.1	0.56	10.0
tb12-8	2.6	23.4	39.5	n.d.	31.1	3.4	0.37	28.4

2-Ring = alkylated aromatics and hydroaromatics composed of two rings
3-Ring = alkylated aromatics and hydroaromatics composed of three rings
4-Ring = alkylated aromatics and hydroaromatics composed of four rings and other polynuclear aromatics
n.d. = not determined
B+P/≥2-Ring = Benzenes + Phenols/2-Ring + 3-Ring + 4-Ring+
ΣAro/ΣAli = Total Aromatics/ Total Alkanes